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(54) Title: ALKALINE CLEANING FORMULATION CONTAINING A HYDROLYZED SILANE AND METHOD OF APPLYING THE SAME (57) Abstract An alkaline cleaning formulation containing a hydrolyzed trialkoxysilane, a surfactant, an alcohol and water is disclosed. The cleaning formulation is stable, provides excellent cleaning efficacy and deposits a silane coating on the surfaces to which it is applied to leave a protective coating thereon. Also disclosed is a method for applying the cleaning formulation to hard surfaces covered by water.		

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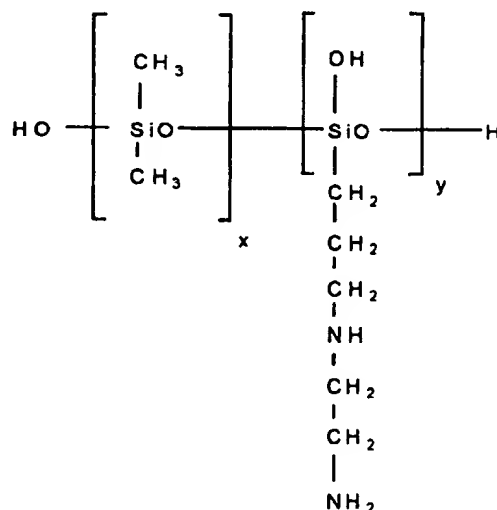
ALKALINE CLEANING FORMULATION CONTAINING A HYDROLYZED SILANE AND METHOD OF APPLYING THE SAME

5 Technical Field

This invention relates to an alkaline cleaning formulation containing a hydrolyzed trialkoxysilane. The formulation is applied to hard surfaces to clean the surface and provide a uniform silane coating on the cleaned surface. The invention also relates to a method for applying the alkaline cleaning formulation of this
10 invention to hard surfaces covered by water.

Background Art

It is known to apply silane cleaning solutions to surfaces to impart water repellency and provide a protective barrier on the treated surface. For example,
15 U.S. Patent No. 4,948,531 discloses an aqueous cleaning composition comprising (a) one or two nonionic surfactants and an amphoteric surfactant as cleaning agents, (b) lecithin and an aminofunctional polydimethylsiloxane copolymer as protective barrier components, (c) one or two glycols as solvency and grease cutting agents, and (d) water. The disclosed aminofunctional polydimethylsiloxane copolymer has
20 the formula:



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and is available as Dow Corning 531 Fluid (Dow Corning Corporation, Midland, Michigan) which is a 50% solution in aliphatic solvents and isopropyl alcohol. This composition is said to clean a surface and simultaneously leave a protective barrier on the cleaned surface.

5 U.S. Patent No. 4,859,359 is directed to a hard surface cleaning and polishing composition comprising a solvent mixture of a glycol ether, a lower aliphatic alcohol, a hydrocarbon solvent and a minor amount of water together with an organic polysiloxane, a silane and a polycarboxylic chelating acid. The silane compound, which is said to promote the solubility of the other silicone compounds
10 in the mixture, is represented by the formula:



wherein R^3 is an alkyl radical containing one to three carbon atoms or phenyl and R^4
15 is an alkyl radical containing one or two carbon atoms. The alkyl trialkoxysilanes are disclosed as preferable.

U.S. Patent 5,073,195 is directed to an aqueous solution of a water silane coupling agent, preferably an amino functional silane coupling agent, and an alkyltrialkoxysilane such as methyltrimethoxysilane or isobutyltrimethoxysilane.
20 The composition is used to treat a surface to impart water repellency to that surface.

Alkoxysilanes are known to hydrolyze upon exposure to water to form reactive silanol groups. The silanol group may then condense with a reactive site on a treated surface. However, if the silanol group is available during storage it may
25 self-condense with other silanol groups to form an insoluble polymer. Hydrolysis of silanes in aqueous medium may be reduced by buffering the emulsions to a specific pH range such as disclosed in U.S. Patent No. 4,877,654. This patent describes a buffered aqueous silane emulsion containing a hydrolyzable silane that is hydrolytically stable within a determined pH range, an emulsifier having an HLB
30 value of from 1.5 to about 20, a buffering compound and water. However, a buffered composition restricted to a certain pH range can be particularly limiting to a formulator of cleaning compositions.

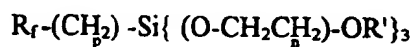
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PCT International Publication No. WO 92/14810 discloses that certain organosilanes containing hydrolyzable groups, especially quaternary ammonium functional organosilanes, can form clear solutions in aqueous media which are stable over extended periods of time by including a water soluble organic, non-silicon

5 quaternary ammonium compound along with nonionic, amphoteric, sarcosine anionic or certain cationic surfactants. The use of hydrolyzed organosiloxanes is not exemplified.

PCT International Publication No. WO 95/23804 is directed to a hydrolyzed silane obtained by emulsifying a hydrolyzable alkoxysilane represented by the

10 formula:

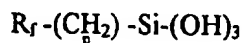


15 wherein R_f is a perfluoroalkyl radical of 3 to 18 carbon atoms, each R' is independently an alkyl radical of 1 to 3 carbon atoms, p is 2 to 4 and n is 2 to 10, with an effective amount of an emulsifier of sufficiently high HLB value to simultaneously retain the hydrolyzable alkoxysilane compound in a substantially totally hydrolyzed state while inhibiting the self-condensation of the hydrolyzed

20 alkoxysilane. Suitable emulsifiers are said to include alkylbenzenesulfonates, linear alkyldiphenyletherdisulfonates, alpha-olefin sulfonates, ethoxylated alkyl alcohol ethers, ethoxylated alkyl alcohol ether sulfates, ethoxylated alkylphenols, ethoxylated alkylphenol ether sulfates, ethoxylated perfluoroalkylalkanols, C_{8-18} alkyltrimethylammonium salts, C_{8-18} alkyldimethylammonium salts, ethoxylated C_{8-18}

25 amine salts, alpha-trimethylamino fatty acid betaines and perfluoroalkyl amphoteric surfactants of the type $R_f-CH_2CH(OR'')CH_2N(CH_3)_2CH_2CO_2$ (inner salt) where R'' is H or acetyl, and quaternary salts of the type $R_f-CH_2CH_2SCH_2CH(OH)CH_2N(CH_3)_3^+Cl^-$. According to PCT International Publication No. WO 95/23804, the alkoxysilanes are believed to be hydrolyzed to

30 hydroxysilanes represented by the formula:



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which do not substantially self-condense when the emulsifier is present.

A similar, but non-fluorinated, alkoxysilane aqueous emulsion is TLF-8291, available from E. I. Du Pont de Nemours and Company, Wilmington, Delaware.

TLF-8291 is believed to contain hydrolyzed C₁₈-alkyltrialkoxysilane (about 10% by weight of the emulsion) in combination with C₈₋₁₈ tetraalkylammonium chloride (about 30 to 40% by weight of the silane) in water. While the hydrolyzed trialkoxysilane aqueous emulsion appears stable as provided, simple dilution of the aqueous emulsion has been found to give a commercially unacceptable cleaning formulation due to poor cleaning efficacy and silane attachment to glass containers holding such a formulation.

Cleaning formulations containing hydrolyzed trialkoxysilanes, such as TLF-8291, which are stable, avoid substantial silane attachment to glass storage containers, provide excellent cleaning, uniform surface deposition after wipe out, and excellent surface wetting and leveling would be highly desirable.

Summary Disclosure Of The Invention

This invention relates to an alkaline cleaning formulation for cleaning hard surfaces comprising: (i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10.0 percent by weight of the formulation; (ii) a surfactant in an amount from about 0.00001 to about 10.0 percent by weight of the formulation, wherein the surfactant is different than the emulsifier; (iii) at least one alcohol having 1 to 12 carbon atoms; and (iv) water. The hydrolyzed trialkoxysilane is preferably formed in an aqueous emulsion from a hydrolyzable trialkoxysilane compound emulsified in water with about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable trialkoxysilane. The emulsifier employed to emulsify the hydrolyzable trialkoxysilane must be in an amount effective to keep the hydrolyzable trialkoxysilane in a substantially totally hydrolyzed state while simultaneously inhibiting appreciable self-condensation of the silane in the aqueous emulsion. The formulation has a pH greater than 7.0 which is generally attained by the addition of a base. Preferably, the alcohol is a mono, di or tri hydric alcohol. The formulation may also include glycol ethers,

solvents, fragrances and any other components well known to those skilled in the art of cleaning formulations.

Another embodiment of the present invention is directed to the above-described cleaning formulation having reduced autophobicity, i.e., the tendency of
5 the formulation to repel itself after application to a hard surface. It has been surprisingly discovered that the autophobicity of the formulations of the present invention can be reduced by the addition of a siloxane to the formulation. Such siloxanes include, for example, polydimethylsiloxane and derivative thereof.

Yet another embodiment of this invention is directed to a method of
10 applying a silane coating to a surface covered by water by adding the above-described alkaline cleaning formulation to the water. It has been surprisingly discovered that the hydrolyzed trialkoxysilane of the formulation of this invention attaches to and modifies the surface of substrates, such as glass, ceramic, fiberglass or porcelain, when applied to the water covering such a surface. It has further been
15 discovered that such surface modification occurs even when relatively low levels of the hydrolyzed trialkoxysiloxanes are added to the water covering such surfaces. This method employing the alkaline cleaning formulations of this invention may be advantageously employed to clean and protect surfaces covered by water, e.g. toilet bowls, with a minimal use of materials and effort.

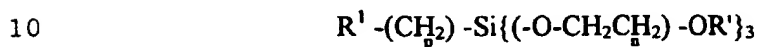
20 The cleaning formulations of this invention are particularly useful for cleaning hard surfaces such as glass, mirrors, tile, ceramic and the like while providing the cleaned surface with a protective silane coating. The formulations of the invention are highly storage stable even when packaged in glass containers, effectively avoid substantial surface attachment of the active silane to the storage
25 container, and thus preserve the active silane for attachment to treated surfaces.

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Modes for Carrying Out the Invention

This invention is directed to an alkaline cleaning formulation which contains a hydrolyzed trialkoxysilane in a stabilized formulation. The hydrolyzed trialkoxysilane is available for attachment to a surface treated with the aqueous alkaline cleaning formulations to form a protective barrier which advantageously inhibits the deposition of soils and grease on the treated surface.

The hydrolyzed trialkoxysilane is derived from a hydrolyzable trialkoxysilane represented by the formula (I):



wherein R^1 is selected from the group consisting of a perfluoroalkyl group of 3 to 18 carbon atoms or an alkyl group of 3 to 24 carbon atoms, and R^2 is independently an alkyl group having 1 to 3 carbon atoms, p is 0 to 4 and n is 2 to 10. Preferably R^1 is an alkyl group of 3 to 24 carbon atoms and p is 0, most preferably R^1 is an alkyl group having 18 carbon atoms and p is 0.

The amount of hydrolyzable trialkoxysilane used in the aqueous emulsion is generally in the range from about 0.00001 to about 25.0 percent by weight of the aqueous emulsion, most preferably from about 0.00001 to about 10.0 percent by weight. Any amount of hydrolyzable trialkoxysilane may be employed in the aqueous emulsion so long as the emulsion is stable prior to its use in preparing the cleaning formulation of this invention.

The hydrolyzed trialkoxysilane may be readily prepared by one of ordinary skill in the art by emulsifying the hydrolyzable trialkoxysilane of formula I in water to form an aqueous emulsion with an emulsifier of sufficiently high HLB value to simultaneously retain the hydrolyzable trialkoxysilane compound in a substantial totally hydrolyzed state and inhibit the hydrolyzed trialkoxysilane compound from appreciable self-condensation. The preparation of aqueous emulsions of hydrolyzed trialkoxysilanes are shown, for example, in PCT International Publication No. WP 95/23804, the disclosure of which is incorporated by reference herein. It may also be possible to form the hydrolyzed trialkoxysilane insitu by the admixture of a

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hydrolyzable trialkoxysilane with the other components of the formulation of this invention.

If present, the emulsifier generally has an HLB ("The HLB System" published by ICI America's Inc., Wilmington, Delaware) value greater than 12.

- 5 However, when a non-fluorinated trialkoxysilane is employed, then preferably the HLB value of the emulsifier is greater than 16, more preferably greater than 18. Compatible emulsifiers may be used in admixture as long as each meets the above-defined HLB requirements.

- Emulsifiers that are preferred for use with a non-fluorinated trialkoxysilane
10 include, without limitation, C₈₋₁₈ alkyltrimethylammonium quaternary salts, alkali metal alkylbenzene-sulfonates, linear alkyl diphenyletherdisulfonates, alpha-olefin sulfonates, alkyl and alkylether sulfates, C₁₂₋₁₈ alkyl dimethylammonium salts, polyethoxylated C₁₂₋₁₈ alkylammonium salts and highly ethoxylated alkyl and aryl alcohols. Such emulsifiers include, for example, hexadecyltrimethylammonium
15 chloride, the sodium salt of C₁₄₋₁₆ alpha olefin sulfonate, octadecylamine-60 E.O. and octadecyldimethylammonium chloride.

- A particularly preferred emulsifier, particularly for use with a hydrolyzed trialkoxysilane where R¹ is a C₁₂ to C₂₄ alkyl group, is an ethoxylated C₈₋₁₈ amine salt, more preferably tetraalkylammonium chloride, most preferably, having
20 predominantly C₁₆-alkyl groups.

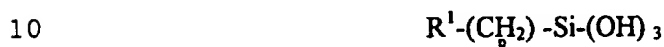
Generally, about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable alkoxy silane is employed in the aqueous emulsion.

- When R¹ is a alkyl group of 3 to 24 carbon atoms then preferably the emulsifier is present in an amount of 10 to 50% based on the weight of the silane, most
25 preferably 30 to 40%. A particularly preferred commercially available hydrolyzed trialkoxysilane emulsion is previously described TLF-8291, available from E.I. Du Pont de Nemours and Company (Wilmington, Delaware).

- Typically, the aqueous emulsion containing the hydrolyzed trialkoxysilane and emulsifier is present in the cleaning formulation in an amount from about
30 0.0001 to about 1.0 percent by weight of the cleaning formulation, most preferably from about 0.0001 to about 0.1 percent by weight. The amount of aqueous

emulsion used in the cleaning formulation will, of course, depend on the concentration of the hydrolyzed trialkoxysilane in the aqueous emulsion. Thus, any amount of aqueous emulsion may be employed that provides an effective amount of hydrolyzed trialkoxysilane in the cleaning formulation to change the hydrophobicity of a treated surface by surface attachment of the hydrolyzed trialkoxysilane.

Not wanting to be bound by any theory, but so as to provide a full disclosure, it is believed that the hydrolyzed trialkoxysilane is represented by (i) the formula (II):



wherein R^1 and p are the same as described for formula I, (ii) by oligomers of formula II or (iii) mixtures thereof. The hydrolyzed trialkoxysilane may form oligomers by the self-condensation of the silanol groups of two or more hydrolyzed trialkoxysilanes so long as the oligomer remains soluble in the aqueous emulsion.

Again, without wishing to be bound by any theory, it is believed that the hydrolyzed trialkoxysilane forms a micelle in conjunction with the emulsifier and that after this aqueous emulsion is diluted into a cleaning formulation the hydrolyzed trialkoxysilane is further protected and stabilized by the addition of the surfactants used in this invention in combination with at least one alcohol having 1-12 carbon atoms and by adjusting the pH of the formulation to an alkaline pH. This cleaning formulation allows delivery of the silane to a surface with excellent surface orientation after evaporation of the aqueous carrier. In addition, it is believed that the surfactant inhibits the silane, while in solution, from substantial surface attachment to the storage container and thus preserves the reactive silane for attachment to the treated surface upon application.

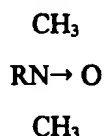
The surfactants employed in the formulation of this invention are selected from the group consisting of: nonionic surfactants such as, for example, linear ethoxylated alcohols (e.g., Neodol® 25-7 (C12-C15 alcohol, EO 7), Neodol® 23-6.5 (C12-C13 alcohol, EO 6.5), Neodol® 1-7 (C12-C13 alcohol, EO 7), Neodol® 25-9 (C12-C15 alcohol, EO 9), Neodol® 45-7 (C14-C15 alcohol, EO 7), or Neodol® 91-6 available from Shell Chemical Co., Houston, Texas, Surfonic® L12-

8 (C11-C12 alcohol, EO 8), Surfonic® L12-6 (C11-C12 alcohol, EO 6), Surfonic® L24-6.5 (C12-C14 alcohol EO 6.5), Surfonic® L24-7 (C12-C14 alcohol, EO 7), Surfonic® L24-9 (C12-C14 alcohol, EO 9) or Surfonic® 108-83-5 available from Huntsman Corp., Austin, Texas), alcohol ethoxy carboxylic acids (e.g., Neodox® 5 23-7, Neodox® 25-6 or Neodox® 45-7) or other nonionic surfactants (e.g., Brij® 76 (polyoxyethylene (20) stearyl ether) or Brij® 97 (polyoxyethylene (10) oleyl ether) available from ICI Americas, Wilmington, Delaware, Pluronic® L-44 (block copolymers of propylene/ethylene oxide) available from BASF, Parsippany, New Jersey, Berol® 223 (fatty amine ethoxylate) available from Berol Nobel, Stratford, 10 Connecticut, and Zonyl® FS-300 (fluoroalkyl alcohol substituted monoether with polyethylene glycol) available from E.I. Du Pont de Nemours and Co., Wilmington, Delaware; amphoteric, such as betaines (e.g., Emcol® CC37-18 available from Witco, Houston, Texas, Lonzaine® C or Lonzaine® CO (cocamidopropylbetaines) available from Lonza Inc., Fairlawn, N.J., Mirataine® BB (lauramidopropyl 15 betaine), Mirataine® CB, or Mirataine® BET C-30 (cocamidopropyl betaines) available from Rhone-Poulenc, Cranbury, New Jersey, Monateric® CAB available from Mona Chemical Co., Paterson, New Jersey and Witco DP 5C-5298-53 (C10 dimethyl betaine) or Witco DP SC-5298-49 (C8 dimethyl betaine) available from Witco), sultaines (e.g., Mirataine® ASC (alkyletherhydroxypropylsultaine) or 20 Mirataine® CBS (cocoamidopropylhydroxysultaine) available from Rhone Poulenc, Lonzaine® CS or Lonzaine® JS (cocoamidopropylhydroxysultaines) available from Lonza Inc., Fairlawn, N.J. and Rewoteric® AM CAS (cocoamidopropylhydroxysultaine) available from Witco), or imidazoline amphoteric (e.g., Amphoterger® W (cocoamphoacetate), Amphoterger® W-2 25 (cocoamphodiacetate), Amphoterger® K (cocoamphopropionate), Amphoterger® K-2 (cocoamphodipropionate), Amphoterger® L (lauroamphodiacetate), Amphoterger® J-2 or Amphoterger® KJ-2 (capryloamphodipropionate) available from Lonza, Rewoteric® AM V (caprylic glycinate), Rewoteric® AM-KSF (cocoamphopropionate) or Rewoteric® AM 2L (lauroamphodiacetate) available 30 from Witco, Phosphoteric® T-C6 (dicarboxyethyl phosphoethyl imidazoline), Monateric® Cy-Na or Monateric® LF-Na available from Mona, and Miranol®

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C2M (cocoamphodiacetate), Miranol® J2M (capryloamphodiacetate), or Miranol® JAS (imidazoline amphoteric) available from Rhone-Poulenc); and cationic surfactants such as amine oxides (e.g., Barlox® LF, Barlox® C, Barlox® 105, Barlox® 12, Barlox® 16S, or Barlox® 18S available from Lonza, 5 Rhodamox® LO or Rhodamox® CO available from Rhone-Poulenc and Varox® 305 or Varox® 743 available from Witco), and quaternary cationic surfactants (e.g., Bardec® 208M or Barquat® 42802 available from Lonza and BTC 835 available from Stephan, Co., Northfield, Illinois), or dialkoxyl alkyl quaternaries (e.g., Variquat® 66, Variquat® K-1215, Adogen® 444, Adogen® 461 or 10 Adogen® 462 available from Witco).

The particularly preferred amine oxides are represented by the formula:



15 wherein R is a C₈ to C₁₆ alkyl group. Most preferably R is a C₁₁ alkyl group.

The surfactant employed in the formulation of this invention will differ from the emulsifier described above. At least one surfactant must be present, although, it may be preferable to employ more than one surfactant.

Generally the surfactant or mixture of surfactants will be present in the 20 formulation in an amount from about 0.00001 to about 10 percent by weight of the formulation, more preferably in an amount from about 0.0001 to about 5 percent by weight of the formulation and most preferably in an amount from about 0.001 to about 3 percent by weight of the formulation. However, any amount of surfactant may be employed that provides a formulation that contains a stabilized hydrolyzed 25 trialkoxysilane and which has good cleaning properties.

At least one alcohol having 1 to 12 carbon atoms employed in the formulation of this invention was preferably selected from mono, di and tri hydric alcohols. Such mono, di and tri hydric alcohols include, for example, ethanol, propanol, hexanol, isopropanol, N-pentanol, propylene glycol, glycerin, 2-pentanol, 30 3-pentanol, 2-butanol, diethylene glycol, Neodol® 91 (C₉ - C₁₁ primary alcohol), Neodol® 1 (C₁₁ primary alcohol) and decyl alcohol. Generally, the concentration

of the mono, di or tri hydric alcohols in the formulation is in a range from about 0.00001 to about 5.0 percent by weight of the formulation. The amount of alcohol employed in the formulation of this invention should be maintained below that amount which would cause substantial alkylation of the hydrolyzed trialkoxysilane.

5 Besides the alcohols described above, the formulations of this invention may also include other solvents, such as glycol ethers, to assist in cleaning the treated surface. Typical glycol ethers include, without limitation Dowanol® EB, (ethylene glycol n-butyl ether), Dowanol® DB (diethylene glycol n-butyl ether), Dowanol® PnB (propylene glycol n-butyl ether), Dowanol® DPnB (dipropylene glycol n-butyl
10 ether), Dowanol® PPh (propylene glycol phenyl ether), Dowanol® PMA (propylene glycol methyl ether acetate), Dowanol® EPH (ethylene glycol phenyl ether), Dowanol® DPMA (dipropylene glycol methyl ether acetate), Dowanol® DPM (dipropylene glycol methyl ether), Dowanol® PnP (propylene glycol n-propyl ether), Witco® DM-55 (polyethylene glycol dimethyl ether) and the like. If
15 employed, the glycol ethers are generally present in the formulation in an amount from about 0.1 to about 6.0 percent by weight of the formulation.

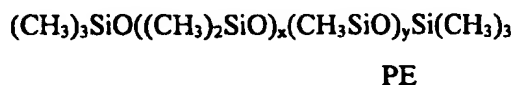
The formulations of this invention typically include a base to ensure that the pH of the formulation is greater than 7, and preferably from about 7.1 to about 13.0, most preferably about 8.5 to about 11.5. Generally such a base is present in
20 an amount from about 0.00001 to about 5.0 percent by weight of the formulation. Exemplary bases include, without limitation, ammonium hydroxide, monoethanolamine, sodium hydroxide, sodium metasilicate and potassium hydroxide. Ammonium hydroxide is preferred.

Additional adjuvants which may be employed in the formulations of this
25 invention include fragrances, colorants and the like. The use of such adjuvants is well known to those of ordinary skill in the art.

The cleaning formulations of the present invention may be prepared by first adding the surfactant to water followed by the addition of the aqueous emulsion containing the hydrolyzed trialkoxysilane. Thereafter, any solvents, bases or other
30 adjuvants may be added to the formulations.

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In yet another embodiment of this invention, a siloxane is added to the above described cleaning formulation to reduce the autophobicity of those formulations. The siloxanes that may be employed include polydimethyl- siloxane and derivatives thereof. Such derivatives may include, for example, polyalkylene
 5 oxide-modified polydimethylsiloxanes represented by the formula



10 wherein PE is represented by $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{EO})_m(\text{PO})_n\text{Z}$ wherein EO is ethyleneoxy, PO is 1,2-propyleneoxy and Z is hydrogen or a lower alkyl group, or



15 wherein PE' is represented by $-(\text{EO})_m(\text{PO})_n\text{R}$ wherein EO and PO are the same as described above and R is a lower alkyl group.

Other siloxanes which may be useful for reducing autophobicity include aromatic substituted siloxanes such as diphenyldimethylsiloxane copolymers, phenylmethylsiloxane polymers and methyl (propyl hydroxide, ethoxylated) bis
 20 (trimethylsiloxy) silane (Dow Corning® Q2-5211, available from Dow Corning, Midland, Michigan).

If present, the siloxane is employed in an amount effective to reduce the autophobicity of the cleaning formula. Generally, about 0.00001 to about 0.5 percent of siloxane by weight of the formulation may be added to inhibit
 25 autophobicity. However, any amount of siloxane that is effective to inhibit autophobicity is encompassed by the present invention.

This invention is also directed to a method of applying a silane coating on a hard surface, such as glass, ceramic, fiberglass or porcelain, that is covered by water. The above-described alkaline cleaning formulation is added directly to the
 30 water in an amount effective to modify the surface covered by the water through attachment of the silane to that surface.

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Without being bound to theory, it is believed that the silane contained in the formulation of this invention has a preferred orientation for liquid/air or liquid/solid surfaces. After the alkaline cleaning formulation is introduced to the water, it is believed that the hydrolyzed trialkoxysilane is no longer stabilized to inhibit surface
5 attachment and that the reactive silane migrates to the liquid/solid interface and adheres to the surface. It has been surprisingly discovered that surface modification can be obtained with as little as 0.1 ppm to 10 ppm of hydrolyzed trialkoxysilane in the water.

The method of this invention can be readily practiced, for example, by the
10 addition of an effective amount of the alkaline cleaning formulation to water contacting the surface which is to be treated. The amount of alkaline cleaning formulation that is added to the water is dependent on the concentration of hydrolyzed trialkoxysilane in the formulation, the amount of water contacting the surface and the surface area that is to be coated. Generally, the amount of alkaline
15 cleaning formulation added to the water is an amount that will provide at least about 0.01 ppm of hydrolyzed trialkoxysilane in the water.

The alkaline cleaning formulation may be added to the water in any manner desired, such as by direct application or by a slow release mechanism, e.g., a toilet bowl tank dispenser.

20 The Examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

Example 1

A cleaning formulation was prepared containing the following components (as used herein % w/w means the percent weight of the component based on the weight of the formulation):

Components	% w/w
Lonza Barlox®12 (amine oxide) ¹	0.250
Isopropyl Alcohol	3.000
Dow Triad ²	1.000
Fragrance	0.050
n-Hexanol	0.100
Deionized Water	94.396
NH ₄ OH (28.5%)	0.200
TLF-8291 ³	1.000
Colorant	0.004
	100.000
CH_3 ¹ $\text{RN} \rightarrow \text{O}$, wherein R is a C ₁₂ alkyl group CH_3 ² Equal parts of Dowanol PnP, DPM and PnB ³ 10% C ₁₈ -alkyltrialkoxyl silane with C ₁₆ -tetraalkylammonium chloride (30 to 40% based on the silane) in an aqueous emulsion available from E.I. Du Pont de Nemours & Co., Wilmington, Delaware	

The resulting formulation had a clear appearance and a pH of 10.42.

Example 2

10 A cleaning formulation was prepared in a manner similar to Example 1, except the surfactant was Lonza Barlox® 10-S (an amine oxide wherein R is a C₁₀ alkyl group). The formulation had a hazy/cloudy appearance and pH of 10.43.

Example 3

The cleaning formulation was prepared in a manner similar to Example 1, except the surfactant was Lonza Barlox® LF (purified amine oxide wherein R is a C₁₂ alkyl group). This formulation had a slightly hazy appearance and a pH of 10.43.

Examples 4-14

The following cleaning formulations were prepared in a manner similar to Example 1, with the exception that no colorant was used and the Dow Triad was replaced by the glycol ethers set forth in the table below:

Example	Glycol Ether	pH	Appearance
4	PnP	10.49	clear
5	PnB	10.32	clear
6	DPM	10.35	clear
7	DB	10.50	clear
8	EPh	10.46	clear
9	PPh	10.52	hazy
10	DPnP	10.56	clear
11	PMA	10.22	clear
12	PM	10.65	clear
13	DPnB	10.69	clear
14	DPMA	10.51	clear

Examples 15-26

The following cleaning formulations were prepared in a manner similar to Example 1, with the exception that no colorant was used and the n-hexanol was replaced with the following mono, di or trihydric alcohols as set forth in the table below:

Example	Alcohol	pH	Appearance
15	Diethylene Glycol	10.50	clear
16	Glycerine	10.49	clear
17	Isopropanol	10.51	clear
18	Decyl Alcohol	10.48	hazy
19	Neodol® 91	10.34	hazy
20	Propylene Glycol	10.33	clear
21	2-Pentanol	10.70	clear
22	2-Butanol	10.58	clear
23	n-Propyl Alcohol	10.56	clear
24	Ethanol	10.56	clear
25	Hexyl Alcohol	10.62	clear
26	1-Pentanol	10.52	clear

Example 27

A cleaning formulation was prepared in a manner similar to Example 1, with the exception that no colorant was added and 0.250% w/w of a nonionic ethoxylated alcohol, Zonyl® FS-300 (poly(oxy-1,2-ethanediyl, alpha-hydro-omega-hydroxy-ether with alpha-fluoro, omega-(2-hydroxy ethyl) poly(difluoromethylene) also known as fluoroalkyl alcohol substituted monoether with polyethylene glycol), was

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added to the formulation. The resulting formulation had a pH of 10.37 and a clear appearance.

Examples 28-30

- 5 These cleaning formulations were prepared in a similar manner to Example 1, except that no colorant was added and the ammonium hydroxide was replaced by the following bases at the concentrations indicated in the table below:

Example	Base	Amount % w/w	pH	Appearance
28	NaOH(10%)	0.031	10.85	clear
29	KOH(10%)	0.043	10.31	clear
30	NaSiO ₃ ·5H ₂ O	0.015	10.89	clear

10

Example 31

A cleaning formulation was prepared containing the following components:

Components	% w/w
Lonzaine CS (amphoteric sultaine) ¹	0.250
Isopropyl Alcohol	3.000
Dow Triad	1.000
Fragrance	0.050
n-Hexanol	0.100
Deionized Water	94.400
NH ₄ OH (28.5%)	0.200
TLF-8291	1.000
	100.000
¹ sulphobetaine	

The resulting formulation had a pH of 10.55 and a clear appearance.

Example 32

A cleaning formulation was prepared in a manner similar to Example 31,
 5 except that the Lonzaine®CS surfactant was replaced by an amphoteric betaine,
 Lonzaine®CO. The resulting formulation had a pH of 10.56 and a clear
 appearance.

Example 33

10 A cleaning formulation was prepared having the following components:

Components	% w/w
Lonza Amphoterge®KJ-2 (Amphoteric imidazoline)	0.500
Witco Variquat®66(dialkoxo alkyl quaternary) ¹	0.165
Monoethanolamine	0.200
Isopropyl Alcohol	1.250
Lonza Barlox® C12 (amine oxide)	0.100
n-Hexanol	0.050
Fragrance	0.025
NH ₄ OH (28.5%)	0.125
Deionized Water	97.085
TLF-8291	<u>0.500</u>
	100.000
¹ ethyl bis(polyhydroxyethyl)alkyl ammonium ethyl sulfate	

The resulting formulation had a pH of 10.56 and a very slightly hazy appearance.

Examples 34-37

The following formulations were prepared in a manner similar to Example 33 with the exception that the amphoteric surfactant, Lonza Amphoterge®KJ-2, was replaced by the amphoteric surfactants listed in the table below:

Example	Amphoteric Surfactant	pH	Appearance
34	Miranol®C2M ¹	10.54	clear to hazy
35	Amphoterge®W-2 ²	10.70	clear
36	Amphoterge®L ³	10.60	clear
37	Rewoteric AMV ⁴	10.64	clear
1. amphoteric imidazoline disodium cocoampho dipropionate 2. coco based imidazoline dicarboxylate, sodium salt 3. lauryl imidazoline dicarboxylate amphoteric 4. amphoteric glycinate			

5

Examples 38-39

The following formulations were prepared in a manner similar to Example 33 except that the amphoteric surfactant, Lonza Amphoterge®KJ-2, was replaced by the cationic surfactants listed in the table below:

Example	Cationic Surfactant	pH	Appearance
38	Barlox®LF ¹	10.67	slightly hazy
39	Variquat®K-1215 ²	10.53	slightly hazy
1. purified amine oxide having a C ₁₂ alkyl group 2. ethyl bis(polyhydroxyethyl)alkyl ammonium sulfate			

10

Stability Testing

Two ounce (57.7g) samples of each formula were placed in a 100°F
5 (37.78°C.) oven. Each sample was visually monitored each day for two weeks and designated either clear, very slightly hazy, hazy or very hazy. The results of these tests are set forth in Table 1. After two weeks, no sample exhibited white clouds in a clear solution which would have been indicative of undesirable polymerization of the silane.

10

Hydrophobicity Testing

Hydrophobicity of each formula treated-surface was measured using a water drop test. This test measures how well a formulation treated-surface repels water. The test was conducted by first cleaning a mirror plate (12 in²
15 (about 77 cm²) Mirror Model #P1212-NT, Monarch Mirror Co.) with HPLC grade acetone and a paper towel. Next, the mirror was rinsed with deionized water and blown dry. The mirror was then divided into 6 equivalent sections and about 0.15 to 0.25 g of a formula was applied to a section and wiped completely dry with half of a paper towel. After waiting one half hour, a pipette was used to deliver five
20 drops of room temperature tap water to each section and to a control section, i.e., a section of the mirror to which a formula was not applied. After 5 minutes, each drop's diameter was measured parallel to the base of the mirror. An average drop size was calculated for each formula and the control.

The average drop size for the formulas tested was found to be 0.70 cm,
25 while the average drop size for the controls was 0.76 cm. Almost every formula exhibited an improvement over the control. The results of the water drop test are set forth in Table 1.

An alternative drop test was employed for several of the formulations of this invention. This test involved substituting dodecane for water in the above-
30 described water drop test. In this test the dodecane was dropped onto the treated surface only three or four minutes after the formula was applied and the drop was

measured after only two or three minutes. The results of this test are set forth in Table 1.

Sliding Drop Test

- 5 The sliding drop test, which quantifies how a droplet flows or wets an inclined surface, was conducted on several of the formulations of this invention. The test was conducted on a 6 in² (about 15 cm²) glazed ceramic tile (Tilepak Glossy White CC-100), which was first cleaned with warm tap water and wiped dry. Each tile was treated with an equivalent amount of formulation (two to ten
- 10 drops) and wiped dry. After ten minutes the ceramic tile was placed on an incline and a Gilson Pipetman was used to dispense a 50 µmL drop on each tile. The trail left on the tile was observed and rated on a scale of 0-5 as follows:
- 0 - indicates a continuous even trail the same width as the drop;
 - 1 - indicates a continuous trail narrower than the drop;
 - 15 2 - indicates a trail that is occasionally broken and narrower than the drop;
 - 3 - indicates a trail with only half the trail wetted;
 - 3.5 - indicates that elongated drops cover a quarter of the trail;
 - 4 - indicates that spherical drops cover a quarter of the trail;
 - 4.5 - indicates that the trail consists of only a few scattered spherical drops; and
 - 20 5 - indicates the drop rolls off the tile leaving no trail.

The results of this test are set forth in Table 2.

Cleaning Tests

- A cotton swab cleaning test was also utilized to test the cleaning efficacy of
- 25 the formulations of this invention, versus interior soil, shell soil, beef tallow and various permanent ink markers.

Interior soil was prepared by adding and melting together 0.5g of synthetic sebum, 0.5g of mineral oil, and 0.5g clay, followed by the addition of 98.5g of 1,1,1-trichloroethane. (Synthetic sebum consists of: 10% palmitic acid; 5% stearic

30 acid; 15% coconut oil; 10% paraffin wax; 15% cetyl esters wax; 20% olive oil; 5% squalene; 5% cholesterol; 10% oleic acid; and 5% linoleic acid which are added

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together and heated over low heat in order to melt the solids and form a homogeneous mixture.) Shell soil consists of 40 parts Metallic Brown Oxide (Pfizer B-3881); 24 parts Kerosene (deodorized); 24 parts Shell sol 340; 2 parts White Mineral Oil; 2 parts Shell Tellus 27; and 2 parts Hydrogenated Vegetable Oil (Crisco). The Shell soil was prepared by dissolving vegetable shortening (Crisco) in kerosene and Shell Sol 340. Next, mineral oil, Shell Tellus 27 and pigment were added followed by agitating continuously for two hours.

A mirror plate, like that employed in the hydrophobicity test, was cleaned with Classical EB Windex® and thoroughly dried with a paper towel. The soils were applied to the mirrors. After 24 hours, a cotton swab was dipped into the formulations and wiped horizontally in a constant motion ten cycle pattern, about one inch (2.54 cm) long, with a constant pressure. After the cleaned areas were dry, the effectiveness of each formula was rated on a scale of one to ten, with one representing no soil removal. The results of the cleaning tests on the formulations of this invention are set forth in Table 1.

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Table I

Ex.	Drop Tests		Cleaning Test				Appearance at 100°F (about 38°C.)
	water	dodecane	Interior	Shell	Beef Tallow	Marker	
1	0.67	1.15	6.0	3.0	5.0	4.1	clear
3	0.68	-	3.5	3.0	7.0	5.4	hazy
4	0.67	-	3.0	3.0	4.0	6.0	s. hazy
5	0.72	-	4.0	3.0	4.0	6.2	v.s. hazy
6	0.68	-	5.0	4.0	3.5	6.1	s. hazy
7	0.72	-	5.0	4.0	3.5	6.1	v.s. hazy
8	0.70	-	4.0	6.0	3.5	5.1	clear
9	0.66	-	4.0	5.0	6.5	5.6	v.s. hazy
10	0.67	-	4.0	5.0	3.5	5.6	v.s. hazy
11	0.66	-	5.0	2.5	3.5	4.0	clear
12	0.66	-	5.0	4.0	5.0	5.0	v.s. hazy
13	0.66	-	3.0	3.0	4.0	5.7	clear
14	0.68	-	4.0	6.0	3.5	5.0	clear
15	0.79	1.40	3.0	3.0	4.0	5.5	hazy
16	0.74	1.13	3.0	3.5	4.0	5.5	hazy
17	0.71	-	5.0	3.0	5.0	5.9	hazy
20	0.76	-	3.5	5.5	3.0	4.4	hazy
21	0.70	-	3.0	4.0	4.0	6.8	hazy
22	0.74	-	3.0	3.0	4.0	6.1	hazy
23	0.70	-	4.0	4.5	4.0	6.3	hazy
24	0.69	-	3.5	4.0	4.5	6.2	hazy
25	0.70	-	3.0	4.0	6.0	5.9	hazy
26	0.72	1.64	3.0	4.5	4.5	5.9	hazy
27	0.66	-	6.0	3.0	4.0	5.7	v.s. hazy
28	0.62	1.39	6.0	7.0	7.0	6.3	s. hazy
29	0.64	1.25	8.0	6.0	7.0	7.1	s. hazy
30	0.61	-	7.0	6.0	6.0	7.0	hazy
31	0.64	1.33	6.0	6.0	5.0	6.9	clear
32	0.65	-	7.0	6.0	6.0	6.8	hazy
33	0.76	-	6.0	6.0	2.0	6.4	v.s. hazy
34	0.65	-	5.0	4.0	4.0	7.4	clear
35	0.72	-	6.0	3.0	3.5	6.6	clear
36	0.70	-	5.0	3.0	3.0	7.3	clear
37	0.74	-	4.0	4.0	3.0	7.2	v. hazy
38	0.81	-	5.0	4.0	3.0	7.2	hazy
39	0.85	-	3.0	5.0	2.0	7.3	v. hazy
Control	Avg. 0.75	Avg. 2.12	-	-	-	-	-

Table 2

Example	Sliding Drop Test (10 drops)
1	4.5
15	4.5-5
16	4.5
26	5.0
28	4.5
29	5.0
31	5.0

Even after two weeks at 100°F (about 38°F.), none of the formulas of this invention developed a white cloudy appearance in a clear solution that would have been indicative of the formation of insoluble polymer due to silane instability. However, the results illustrate that certain formulations remained clearer than others. In particular, Examples 1, 3, 8, 11, 14, 31, 34, 35 and 36 exhibited excellent clarity.

The results of the water drop test set forth in Table 1 show that almost all the formulations of this invention increased the hydrophobicity of the treated surface. Examples 28-32 and 34 exhibited particularly strong hydrophobicity (0.61-0.65 versus a 0.75 average for the control), while Examples 1, 3, 4, 6, 9-14, 24 and 27 showed moderately strong hydrophobicity improvement (0.66-0.69 versus a 0.75 average for the control). The dodecane drop tests on Examples 1, 15, 16, 26, 28, 29 and 31 show that all the tested formulations improved the solvophobicity of the treated surface (1.13 to 1.64 versus the control average of 2.12).

Notwithstanding a formulation's ability to deliver a protective silane coating and render a surface hydrophobic, the formulation should also have the

ability to clean. The cleaning test results illustrated in Table 1, show that Examples 28-32 are particularly strong overall for each of the soil groups. Other formulations evidence strong cleaning properties for a particular soil group. Thus, the results of these tests indicate that the formulations of this invention are not only stable and
5 provide a protective silane coating, but also provide effective cleaning efficacy, the scope of which can be modified depending on the nature of the formulation.

The results set forth in Table 2, also confirm that the formulations of Examples 1, 15, 16, 26, 28, 29 and 31 rendered the surface of ceramic tiles treated with those formulations hydrophobic or water repellant.

10

Industrial Applicability

The cleaning formulations of this invention are highly storage stable even when packaged in glass containers, and therefore conserve the active silane for
15 attachment to treated surfaces. In addition, the method of applying the alkaline cleaning formulations of this invention may be advantageously used to clean and protect water covered surfaces with a minimal use of materials and effort.

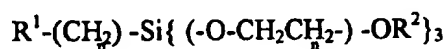
Other variations and modifications of this invention will be obvious to those skilled in this art. This invention is not to be limited except as set forth in the
20 following claims.

WHAT IS CLAIMED IS:

1. An alkaline cleaning formulation for cleaning hard surfaces comprising:
 - (i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10.0 percent by weight of said formulation;
 - (ii) a surfactant in an amount from about 0.00001 to about 10.0 percent by weight of said formulation;
 - (iii) an alcohol having 1 to 12 carbon atoms; and (iv) water, wherein said formulation has a pH greater than 7.0.

- 2) An alkaline cleaning formulation according to claim 1, wherein said hydrolyzed trialkoxysilane is formed in an aqueous emulsion from a hydrolyzable trialkoxysilane compound emulsified in water with about 5 to 100 percent by weight of an emulsifier based on the weight of the hydrolyzable trialkoxysilane and said surfactant is different than said emulsifier.

3. An alkaline cleaning formulation according to claim 2, wherein said hydrolyzable trialkoxysilane is represented by formula (I):



wherein R^1 is selected from the group consisting of a perfluoroalkyl group of 3 to 18 carbon atoms or an alkyl group of 3 to 24 carbon atoms, each R^2 is independently an alkyl group having 1 to 3 carbon atoms, p is 0 to 4 and n is 2 to 10.

4. An alkaline cleaning formulation according to claim 3, wherein R^1 is an alkyl group having 12 to 24 carbon atoms and p is 0.
5. An alkaline cleaning formulation according to claim 4, wherein said emulsifier is an ethoxylated C_{8-18} amine salt.

6. An alkaline cleaning formulation according to claim 1, wherein said surfactant is selected from the group consisting of nonionic surfactants, amphoteric betaines, amphoteric sultaines, imidazoline amphoterics, amine oxides, quaternary cationics, dialkoxy alkyl quaternaries and mixtures thereof.
7. An alkaline cleaning formulation according to claim 5, where said surfactant is selected from the group consisting of amine oxides, amphoteric sultaines, amphoteric betaines, nonionic ethoxylated alcohols and mixtures thereof.
8. An alkaline cleaning formulation according to claim 7, wherein said surfactant is an amine oxide or an amphoteric betaine.
9. An alkaline cleaning formulation according to claim 1, wherein said alcohol is selected from the group consisting of mono-hydric alcohols, di-hydric alcohols, tri-hydric alcohols and mixtures thereof.
10. An alkaline cleaning formulation according to claim 1, wherein said solvent is hexanol, isopropanol or a mixture thereof.
11. An alkaline cleaning formulation according to claim 1, further comprising at least one glycol ether.
12. An alkaline cleaning formulation according to claim 1, further comprising a base in an amount effective to provide said formulation with a pH greater than 7.0.
13. An alkaline cleaning formulation according to claim 12, wherein said base is selected from the group consisting of ammonium hydroxide, monoethanolamine, sodium hydroxide, sodium metasilicate and potassium hydroxide.

14. An alkaline cleaning formulation according to claim 11, wherein the pH of said formulation is about 7.1 to about 13.0.
15. An alkaline cleaning formulation according to claim 1, further comprising a siloxane in an amount effective to reduce an autophobicity of the cleaning formulation.
16. An alkaline cleaning formulation for cleaning hard surfaces comprising:
- (i) a hydrolyzed trialkoxysilane in an amount from about 0.00001 to about 10 percent by weight of said formulation, wherein said hydrolyzed trialkoxysilane is formed in an aqueous emulsion from a C₁₈-alkyltrialkoxysilane compound emulsified in water with a C₈₋₁₈ tetraalkylammonium chloride in an amount of about 30 to 50 percent by weight of the silane;
 - (ii) a surfactant in an amount from about 0.00001 to about 10.0 percent by weight of said formulation, wherein said surfactant is selected from the group consisting of amine oxides, amphoteric sultaines, amphoteric betaines, nonionic ethoxylated alcohols and mixtures thereof;
 - (iii) at least one mono-hydric alcohol, di-hydric alcohol, or tri-hydric alcohol;
 - (iv) optionally, at least one glycol ether;
 - (v) a base in an amount effective so that said formulation has a pH between 8.5 and 11.5; and
 - (vi) water.
17. An alkaline cleaning formulation according to claim 16, wherein said mono-hydric alcohol, di-hydric alcohol or tri-hydric alcohol is selected from the group consisting of isopropanol, hexanol and mixtures thereof.
18. An alkaline cleaning formulation according to claim 17, wherein said glycol ether is a mixture of propylene glycol n-butyl ether, propylene glycol n-propyl ether and dipropylene glycol methyl ether.

19. A method for cleaning and modifying a hard surface covered by water comprising the step of applying an alkaline cleaning formulation according to claim 1, to water contacting said hard surface in an amount effective to modify said hard surface by attachment of said hydrolyzed trialkoxysilane to said surface.

20. A method according to claim 19, wherein the concentration of said hydrolyzed trialkoxysilane in said water is from about 0.01 ppm to about 10,000 ppm.

INTERNATIONAL SEARCH REPORT

Inter. Appl. Application No
PCT/US 97/05125

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/16 C11D3/43

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 14810 A (JOHNSON & SON INC S C) 3 September 1992 cited in the application see page 22, paragraph 1; claims; examples 1,32,34 ---	1
A	WO 95 23804 A (DU PONT) 8 September 1995 cited in the application see page 7, line 18 - line 19; claims; examples ---	1-3,5
A	EP 0 279 623 A (DOW CORNING) 24 August 1988 see page 5, line 2 - line 9; claim 22 see page 6, line 2 - line 14 see page 12, line 41 - line 65 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 249 550 A (N.T. METTERS) 3 May 1966 see claims; examples -----</p>	1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/05125

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9214810 A	03-09-92	AU 655621 B	05-01-95
		AU 9144691 A	15-09-92
		CA 2100670 A,C	16-08-92
		EP 0640122 A	01-03-95
		JP 6505036 T	09-06-94
		KR 9615974 B	25-11-96
		US 5411585 A	02-05-95

WO 9523804 A	08-09-95	US 5550184 A	27-08-96
		AU 1937695 A	18-09-95
		EP 0748323 A	18-12-96
		US 5552476 A	03-09-96

EP 0279623 A	24-08-88	US 4842766 A	27-06-89
		AU 595983 B	12-04-90
		AU 1190688 A	18-08-88
		CA 1309314 A	27-10-92
		DE 3882246 A	19-08-93
		DE 3882246 T	03-02-94
		JP 63232837 A	28-09-88
KR 9610077 B	25-07-96		

US 3249550 A	03-05-66	NONE	
